Concerted or Stepwise Mechanism for Acetylation of 3-Methylphenol? Computational Determination of Activation Energies

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It is not entirely clear whether the nucleophilic acyl substitution of phenolate is a stepwise reaction or instead undergoes a concerted process. The reaction used the B3LYP and MPW1K algorithms, each with the basis set 6-31+G**. Low-energy conformers of the putative tetrahedral intermediate were generated with a Systematic conformational search. The low energy conformers were optimized, giving one lowest energy conformation to be used as the tetrahedral intermediate. The barriers for the decomposition of the tetrahedral intermediate were found by lengthening either the C_4-O_5 or C_4-O_3 bond (see **Figure 1**) in the intermediate until a clear maxima, or transition state, was found. The MPW1K barriers were 6.18 and 6.45 kJ/mol for the forward and reverse reactions, respectively, while the B3LYP barriers were 0.69 and 1.83 kJ/mol. The two prominent maxima at each transition state indicated a stepwise reaction for both calculation methods.

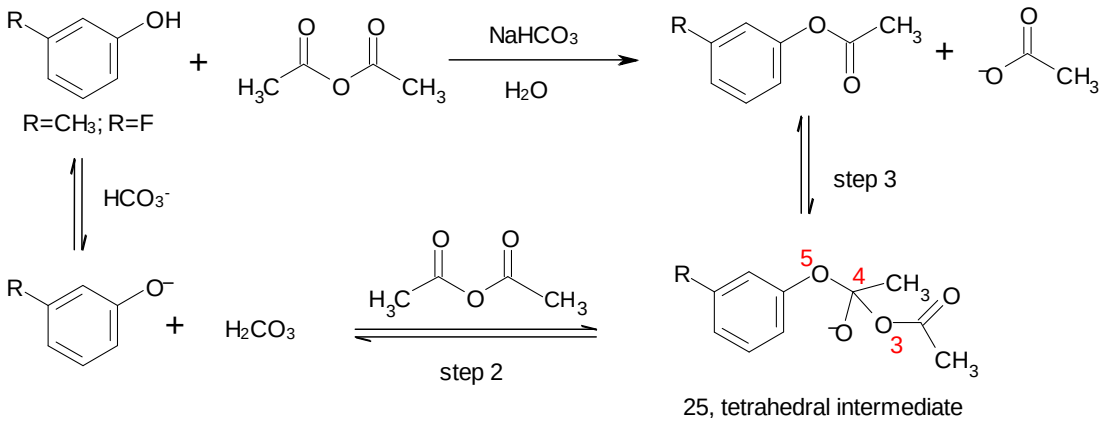

Figure 1: The acetylation of 3-Methylphenol by acetic anhydride in aqueous sodium bicarbonate.